A

Textbook of

ENVIRONMENTAL CHEMISTRY

[For B.Sc., B.Sc.(Hons.) and M.Sc. Students]

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by

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Preface

In many universities, environmental chemistry has been introduced as a paper at the undergraduate as well as the post-graduate level. But there are very few books on this subject. Therefore, an attempt has been made to write the book on the said subject. The order of the topics covered in this book may not be able to satisfy every one. Therefore, the order of the topics covered in this book can do some justification for students. Each topic covered in this book is self-sufficient in itself and is well-explained with numerous figures. Further an attempt has been made to describe each topic in the light of modern developments in a simple language and elegant style. An attempt is also made to include the latest developments in the instrumentation of various analytical techniques which are being used for environmental analysis.

We would like to thank several of my immediate colleagues and friends for making useful suggestions during the preparation of manuscript.

Suggestions or criticism towards the further improvement of the book shall be gratefully acknowledged.

The Authors

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Introduction to Environmental Chemistry

1.1. Meaning of Environment

Environment is taken to mean all those which are physical and chemical, organic and non-organic components of the atmosphere, lithosphere and oceans. Environment is the aggregate of external conditions that influence the life of an individual or population, specifically the life of men ; environment ultimately determines the quality and survival of life. Organisms and environment are in constant change. Some changes are very rapid, others take thousand of years. The relationship between and among the physical envionment (soil, water, air) and organismal environment (plant and animal life) constitutes the study of ecology.

Some workers have used the term micro-environment for designating a functional environment, *i.e.*, specific environment of specific organisms. Literally, this term refers to a small environment. But it has been somewhat a relative term. Therefore, this term is used for the immediate environment of an organism.

1.2. Concept of Environmental Chemistry

In simple words, environmental chemistry may be defined as the study of chemical phenomenon in the environment. A more reasonable definition is "*environmental chemistry refers to the study of the sources, reactions, transport, effects and fates of chemical species in the water, soil and air environment.*"

Environmental chemistry is not a single disciplinary science but a multi-disciplinary science which encompasses many vastly different fields such as chemistry, physics, life sciences, agriculture, medical science, public health, sanitary engineering, etc.

Environmental chemistry is not a new discipline. Excellent work has been done in this field 50 or more years ago. Much of the earlier work was done by non-chemistry groups. In recent years, much of the work on environmental chemistry has been done by chemistry groups.

A basic understanding of the fundamental concepts of environmental chemistry is not only essential for all chemists but also for all non-chemists who are engaged in environmental science and related fields.

Environmental chemistry is not just the same old chemistry with a different cover and title on the book but it is more complicated and difficult than pure chemistry because it deals with natural systems which are difficult to understand.

1.3. Scope of Environmental Chemistry

One of the main objective of environmental chemistry is to determine the nature and quantity of specific pollutants in the environment. The difficulty of analysing for many environmental pollutants is that their amount in natural samples is appreciably small, *e.g.*, the levels of air pollutants may be less than a microgram per cubic nature of air, and the levels of many water pollutants may be a part per million by weight or even less than this. Thus, it is evident that environmental chemist requires high sensitivity and accuracy in determining such environmental systems.

Environmental chemistry is not however, the same as analytical chemistry. In order for chemistry to make a maximum contribution to the solution of environmental problems, the chemist must work toward an understanding of the nature, reactions and transport of chemical species in the environment. Analytical chemistry is a fundamental and crucial part of that endeavor but is no means all of it.

1.4. Nomenclature

(1) Environmental Pollution

For the first time in his entire cultural history, man is facing one of the most horrible ecological crisis—the problem of pollution of his environment which sometime in past was pure, virgin, undisturbed uncontaminated and basically quite hospitable for him.

> "*Environmental pollution may be defined as the unfavourable alteration of our surroundings, wholly or largely us a by-product of man's actions, through direct or indirect effects of changes in energy patterns, radiation levels, chemical and physical constitution and abundances of organisms. These changes may affect man directly or through his supplies of water and of agricultural and other biological products, his physical objects or possessions, or his opportunities for recreation and appreciation of nature.*"

The most vital and controversial question left unanswered by this definition of environmental pollution has been the question of what constitutes an "unfavorable alteration." Any man-made alteration of the environment probably is having unfavorable effects, at least in the opinion of some people, and favorable effects in the opinion of others, like those whose livelihood depends on an activity that produces pollution. The determination of the extent of the favorable versus unfavorable effects—or of benefits versus costs—has been difficult just because it has been ultimately subjective, even though objective data may get involved in the determination.

The affluent societies of the developed nations of the world have been likely to be more concerned about the unfavorable effects than those nations in which poverty and hunger are major unsolved problems.

Poverty, starvation, and pollution all reflect mankind's failure to design social and political institutions which are capable of properly assessing and controlling technological innovations. Serious problems of poverty and hunger exist in the advanced countries like USA, UK, USSR, etc., despite the progress of the last several decades, and the progress that has been made has been accompanied by the aggravation of many existing environmental problems and the production of new ones.

Natural and Man-Generated Pollution

Many pollutants that concern man occur in nature, although chlorinated hydrocarbons (such as DDT) and certain short-lived radioactive isotopes have been exceptions. In soms cases, the environmental levels have been largely due to natural sources, while in others the levels have been largely produced by man's activities. Table 1-1 gives many examples. Even when natural sources have been more important on a global scale, man-generated pollutants may be more important in urban and industrial areas where the adverse effects of pollution are most severe. It thus becomes important to distinguish between large-scale production of pollutants and local production over a few tens or hundreds of square kilometers.

Table 1.1. Natural versus man-generated pollution.

Almost completely man-generated	
	Chlorinated hydrocarbons (DDT, etc.)
	Lead aerosols
Substantially man-generated	
	Oil on the oceans
	Phosphates in running waters
Substantial contributions from natural sources	
	Hydrocarbons in the atmosphere
	Radiation
	Sulfurr oxides in the atmosphere

Types of Pollution. The usual practice to classify pollution is done according to the environment (air, water, soil) in which it occurs or according to the type of pollutant (lead, mercury, carbon dioxide, solid waste, noise, biocide, heat, etc.) by which pollution has been caused.

Sometimes, pollution is made to classify into two broad categories :

(*a*) *Natural pollution*. It originates from natural processes.

(*b*) *Artificial pollution*. It originates due to activities of man.

However, the following types of pollution have been noticed.

1. Air Pollution
2. Water Pollution
3. Solid Waste Pollution
4. Land Pollution
5. Marine Pollution
6. Noise Pollution
7. Radiation Pollution
8. Thermal Pollution

(2) Pollutants

A pollutant may be defined as any thing, living or not living, or any physical agent (*e.g.*, heat, sound) that in its excess makes any part of the environment undesirable ; if water, undesirable ; for drinking, recreation, visual enjoyment, or as a habitat for the aquatic life normal to it ; if air, undesirable for breathing, for the condition of buildings and monuments exposed to it, or for animal and plant life ; if soil and land, undesirable for raising food and fiber, animals, or for recreation or aesthetic enjoyment. In common usage, "pollutant" is a term which is applied usually to non-living, man-made substances or other nuisances, and it refers to their being in excess in a particular location. Generally the same substances are produced by natural causes, and sometimes in far greater quantities. Oxides of sulphur and nitrogen, particulates and carbon monoxide, for example, all air pollutants, are all produced naturally. Generally, however, those made by nature get widely dispersed, are at low concentrations, and are not by themselves principal threats in congested urban areas. The excesses produced by human activities are the threats.

According to "The Indian Environment (Protection), Act 1986", *a pollutant has been defined as any solid, liquid or gaseous substance present in such concentration as may be or tend to be injurious to environment.*

Further, the unserviceable or residues of things which we manufacture, use and throw away are also regarded as pollutants.

Units of Concentration of Pollutants

Concentrations of pollutants have been usually expressed by fractions. A concentratton of one part per million (1 ppm) means one part pollutant per one million parts of the gas, liquid, or solid mixture in which the pollutant is found. In the case of a gas mixture, the reference is generally to ppm by *volume*, while in the case of liquids and solids the reference has been generally to ppm

Table 1.2. Fractional concentrations.

Symbol	*Definition*	*Fraction*
ppm	Parts per million	10^{-6}
pphm	Parts per hundred million	10^{-8}
ppb	Parts per billion	10^{-9}
ppt	Parts per trillion	10^{-12}

by *weight*. More recently, it has become customary to express gaseous pollutants and particulate matter in the atmosphere in mass density units of micrograms per cubic meter ($\mu g/m^3$), and in this case it has been necessary to specify the temperature (usually 0 or 25°C) and pressure (usually 1 atm) at which the concentration is expressed. Table 1-2 lists some common fractional concentrations.

Types of Pollutants

Certain common pollutants of well-developed and developing countries are as follows :

(*i*) **Gaseous pollutants.** Oxides of nitrogen (particularly, nitric oxide, No ; nitrogen dioxide, NO_2) SO_2, H_2S, CO, halogens (chlorine, bromine, iodine), etc.

(*ii*) **Fluoride compounds**

(*iii*) **Metals.** Mercury, lead, iron, zinc, nickel, tin, cadmium, etc.

(*iv*) **Complex organic pollutants.** Benzene, benzpyrene, acetic acid, ether, etc.

(*v*) **Photochemical oxidants.** Ozone, PAN, PBzN, NO_x, aldehyde, etylene, etc.

(*vi*) **Deposited matter.** Soot, smoke, tar, dust, grit.

(*vii*) **Solid waste.**

(*viii*) **Economic poisons.** Herbicides, fungicides, pesticides, nematocides, insecticides, rodenticides and other biocides.

(*ix*) **Fertilisers**

(*x*) **Radioactive waste**

(*xi*) **Noise**

(*xii*) **Heat**

Some priority pollutants have been listed in Table 1.3.

Table 1.3. Some priority pollutants (UNEP Document Nc 1 G. ½, February, 1947)

Order of pollutant priority		*Medium*
I.	SO_x suspended particles	air
	Strontium, caesium	food
II.	Ozone	air
	DDT and other organo-chlorine compounds	biota, man
III.	Nitrates, nitrites	drinking water
	Oxides of nitrogen	air
IV.	Mercury compounds	food, water
	Lead and CO	food and air
V.	Petroleum hydrocarbons	sea
	Carbon monoxide	air
VI.	Fluorides	water (fresh water)
VII.	Asbestos	air
	Arsenic	drinking water
VIII.	Mycotoxins and micro-bial contaminants	food

However, from the ecosystem viewpoint, the pollutants can be classified into two basic types : **nondegradable pollutants** and **biodegradable pollutants** (**Odum**, 1971). The materials and poisons, like aluminium cans, mercurial salts, long-chain phenolic chemicals and DDT that either do not degrade or degrade only very slowly in the natural environment, are termed as **nondegradable pollutants**. Such nondegradable pollutants not only accumulate but are often "biologically magnified" as they move in biogeochemical cycles and along food chains. Also they frequently react with other compounds in the environment to produce additional toxins. The **biodegradable pollutants** include domestic sewage, heat, etc. The domestic sewage can get rapidly decomposed by natural processes or in engineered systems (like a municipal sewage treatment plant) that enhance nature's great capacity to decompose and recycle. Problems arise with the biodegradable pollutants when their input into the environment get exceeded the decomposition or dispersal capacity.

(3) **Contaminant**

A contaminant may be defined as something which causes a deviation from the normal composition of an environment. Contaminants are not classified as pollutants unless they have some detrimental effect. For instance, chlorine gas escaped from an accidental truck on Ring Road, New Delhi in 1987 killed two persons. This gas is not occurring in nature. Therefore, it is regarded as a contaminant due to its dangerous effect. Further, it is regarded as a pollutant due to its detrimental effect. A contaminant does not occur in nature but gets introduced by human activity into the environment, affecting its composition.

(4) Source

It is generally the logic place from which the pollutant originates. The identity of source is important to eliminate pollution. After a pollutant gets released from a source, it may act upon a receptor.

(5) Receptor

It is anything which is affected by the pollutant. Man is the receptor whose eyes smart from oxidants is the atmosphere. Trout fingerlings are the receptors which may die from exposure to dieldrin in water. Man is the receptor of photochemical smog causing irritation of the eyes and respiratory tract.

(6) Sink

It is the medium which is able to retain and interact with a long-lived pollutant, though not necessarily indefinitely. Thus, a limestone wall may be the sink for atmospheric sulphuric acid, through the reaction

$$H_2SO_4 + CaCO_3 \longrightarrow CaSO_4 + H_2O + CO_2$$

which fixes the sulphate as part of the wall composition. Also, the oceans are sinks for atmospheric carbon dioxide.

(7) Pathway of a Pollutant

It refers to the mechanism by which the pollutant gets distributed from its source into the environmental segments. For example, the tetramethyl lead, present in gasoline/automobile gets distributed in nature by following the pathway given below :

$$Pb(C_2H_5)_4 \xrightarrow{\text{Autoexhausts}} PbCl_2 + PbBr_2 \text{ (Released into air)}$$

$$\downarrow$$

$$\text{To food crops and food chain} \longleftarrow PbCl_2 + PbBr_2 \text{ (Soil)}$$

(8) Speciation

The term is used for the different chemical forms or species of inorganic or organo-metallic compounds which are present in the environment. It becomes essential to identify the chemical species of a pollutant because some species have been found to be toxic than others. For example, the species such as $(CH_3Hg)^+$ and $(CH_3)_2$ Hg have been found to be deadly poisonous as compared to other species of mercury.

(9) Dissolved Oxygen

Oxygen dissolved in water has been an important vital species which gets consumed by oxidation of organic matter/reducing agent etc. It is regarded as an important water quality parameter. Its optimum value for good quality water has been 4-6 mg/litre of dissolved oxygen (DO) which is able to maintain aquatic life in a water body. If DO values are somewhat lower than this value, this indicates water pollution.

(10) Biochemical Oxygen Demand (BOD)

It is a water quality parameter for organic matter in water, which is empirical in nature. It may be measured by the quantity of oxygen utilised by suitable aquatic microorganisms during a five-day period.

Biochemical oxygen demand (BOD) has been a standardized measurement of the amount of oxygen that would be required by microorganisms to cause the decomposition of certain organic and inorganic matter in the water. The measurement is done under standardized conditions (*e.g.*, at 20°C and 5 days to allow the decomposition to take place). The result is called the 5-day BOD and is expressed in milligrams of oxygen per litre of water. BOD is not a pollutant but an indicator. It measures no particular substance but a family—any substance that microorganisms can consume (using oxygen as they do) or any material attacked under the conditions of the test. The substances decomposed in the test may be food used by the microorganisms or certain chemicals that are readily attacked by oxygen, perhaps with the aid of enzymes released by the microorganisms. These chemicals include sulphites and sulphides (from paper mills), ferrous iron, and some easily oxidized compounds. Many organics, however, make no contribution to the BOD but still render the water unfit for human use. BOD values of several hundred milligrams per litre characterize "strong" sewage. For "excellent" drinking water the 5-day BOD, on a monthly average, should be in the range of 0.75—1.5 milligrams/litre. BOD values are important when they signify that the oxygen supply dissolved in the water will be so greatly reduced that desirable fish no longer can survive or when they signify that conditions for the propagation of dangerous bacteria exist.

(11) Chemical Oxygen Demand

It is an important water quality parameter. It is an index of the organic content of water oxygen demanding substances in water.

The chemical oxygen demand (COD) has been a measure of the concentration in a water supply of substances that can get attacked by a strong chemical oxidizing agent in a standardized analysis. (Dichromate oxidation is commonly used). The results of the analysis are usually expressed in terms of the amount of oxygen that would be needed (in principle, because oxygen is not itself used) to oxidize the contaminants to the same final products obtained with the standardized analysis. COD values do not get necessarily correlated with BOD values. Textile wastes, paper mill wastes, and other wastes with high levels of cellulose have COD values considerably higher than their BOD values as cellulose is not readily attacked in the BOD test. Distillery and refinery wastes often have BODs higher than CODs unless the COD measurement is specially modified. In the nature of the two tests, the BOD of a given water supply is able to decrease faster than its COD.

Chemical oxygen demand (COD) has been found to be more scientific than the traditional empirical concept of Biological oxygen demand (BOD). The test is based on the chemical oxidation of material in water by $K_2Cr_2O_7$ in 50% H_2SO_4.

A comparative account of BOD and COD is given in Table 1.4.

Table 1.4. Comparison of BOD and COD.

Biological Oxygen Demand (BOD)	*Chemical Oxygen Demand (COD)*
(*i*) It may be defined as the amount of oxygen used for biochemical oxidation by microorgnisms in a unit volume of water. This test has been developed for five days at 20°C.	(*i*) It may be defined as the amount of oxygen required by organic matter in a sample of water for its oxidation by a strong chemical oxidant, and is expressed as ppm of oxygen taken from a solution of potassium dichromate in two hours.
(*ii*) As BOD value approximates the amount of oxidi-	(*ii*) This value has been a poor measure of strength of

zable organic matter, it is therefore, used as a measure of degree of water pollution and waste strength.	organic matter as oxygen also get consumed in the oxidation of inorganic matter such as nitrates, sulphates, reduced metal ions, and also that some organic materials like benzene, pyridine and few other cyclic organic compounds do not get oxidized by this test.
(*iii*) BOD values have been useful in process design and loading calculations, measure of treatment efficiency and operation, stream pollution control and in evaluating self purification capacity of a stream.	(*iii*) It has been a very important parameter in management and design of the treatment plants due to its rapidity in determination. Values are taken as basis for calculation of efficiency of treatment plants and also figure in the standards for discharging industrial domestic effluents in various kinds of waters.
(*iv*) Types of microorganmisms, pH presence of toxins, some reduced mineral matter and nitrification process have been the important factors that influence the BOD test.	(*iv*) Presence of toxins and other such unfavourable conditions for the growth of microorganisms are not able to affect COD values.

(12) Threshold Limit Value (TLV)

It refers to the permissible level of a toxic pollutant in atmosphere to which a healthy industrial worker gets exposed during an eight-hour day without getting any adverse effect. TLV values for Be and Zn have been 0.002 and 1.000 mg/m^3 respectively.

(13) Synergism and Antagonism

In many cases the combined effects of two or more pollutants are more severe or even qualitatively different from the individual effects of the separate pollutants—a phenomenon known as *synergism*. Numerous studies have shown that some types of particulate matter, such as aerosols of soluble salts of ferrous iron, manganese, and vanadium, can increase the toxicity of sulphur dioxide. Such an increase in toxicity is usually referred to as *potentiation.* Sometimes the combined effects of two pollutants are less rather than more severe, and this situation is referred to as *antagonism.* Cyanides in industrial wastes are quite poisonous to aquatic life, and in the presence of zinc or cadmium they are extremely poisonous (a synergistic effect), apparently due to the formation of complexes; in the presence of nickel, however, a nickel-cyanide complex that is not very toxic is formed. The occurrence of synergistic effects makes it difficult to study the effects of pollution since so many different pollutants are present in the environment and this makes it hard to predict the effects that might take place when certain air or water quality standards are met.

1.5. Environmental Segments

It is convenient to subdivide environmental chemistry into areas involving the chemistry of the atmosphere, hydrosphere, lithiosphere and biosphere. All matter, from minerals in the outer layers of the earth's crust to relatively stable ions in the upper reaches of the atmosphere may be classified in one of these categories.

(1) Atmosphere

The atmosphere refers to the protective blanket of gases which are surrounding the earth. It is able to sustain life on earth and saves it from the hostile environment of outer space. It is able to absorb most of the cosmic rays from outer space and a major portion of the electromagnetic radiation from the sun. It is able to transmit only near ultraviolet, visible, near infrared radiation (300-2500 nm) and radio waves (0.10-40μ) while filtering out tissue-damaging ultraviolet radiation below about 300 nm.

The atmosphere is subdivided into different regions of varying with altitudes. The most simple division is that of the lower atmosphere extending upto approximately so kilometres above the earth's surface and the upper atmosphere, extending out into space.

The atmosphere plays a vital role in maintaining the heat balance of the earth by absorbing infrared radiation emitted by the sun and re-emitted from the earth.

The major components of the atmosphere include nitrogen and oxygen, while the minor components include argon, carbon dioxide and some trace gases.

The atmosphere has been the source of oxygen (essential for life on earth) and carbon dioxide (essential for plant photosynthesis). It also supplies nitrogen which nitrogen-fixing bacteria and ammonia-manufacturing plants use to yield chemically bound nitrogen essential for life. Furthermore, it has been a vital carrier of water from oceans to land, as part of the hydrologic cycle.

Unfortunately, with progress in science and technology, man is dumping waste materials into the atmosphere, which pose a serious problem for survival of mankind itself on earth.

Atmospheric chemistry varies a good deal with altitude, exposure to solar radiation, pollution load and other factors.

(2) **Hydrosphere**

It refers to water in its various forms. It includes all types of water resources such as oceans, seas, rivers, lakes, streams, reservoirs, glaciers, polar ice caps and ground water (*i.e.*, water below the earth's surface). For the study of environmental chemistry, however, liquid water and the chemistry of the chemical entities therein is of predominant importance.

About 97% of the earth's water supply lies in the oceans, while the high salt content does not allow its use for human consumption. Nearly 2% of the water resource gets locked in the polar ice caps and glaciers, while only 1% is found as fresh water (surface water—rivers, lakes, streams, and ground water) for human consumption and other uses.

The history of ancient civilizations such as growth and decline has been closely linked with the quantum of water supply. The major uses of water include irrigation (30%) and thermal power plants (50%), while other uses include domestic (7%) and industrial consumption ($\sim$12%).

The contamination of surface water takes place by pesticides and fertilizers in agricultural run-off water, human and animal wastes in sewage and industrial wastes. Water-borne diseases occurring due to sewage alone have killed millions of people in many developing countries.

The basis of the aquatic environmental chemistry is a proper understanding of the sources, transport, characteristics and chemical species of water.

(3) **Lithosphere**

It includes the outer parts of the solid earth. In general, the term refers to minerals encarentered in the earth's crust and to the complex and variable mixture of minerals, organic matter, water and air making up soil. In so far as environmental chemistry is concerned, the soil is probably the most significant part of the lithosphere.